

Express Mail No.:

EL622259323US

Date of Deposit: Jan. 28, 2002

APPLICATION FOR UNITED STATES LETTERS PATENT

FOR

FIRE RETARDING POLYPROPYLENE COMPOSITION

2002010 042802

Inventor: Jerry Wagner

Assignee: Compression Polymers Group  
Scranton, PA

Attorneys: Standley & Gilcrest LLP  
Attn.: Jeffrey S. Standley  
495 Metro Place South  
Suite 210  
Dublin, Ohio 43017  
Telephone: (614) 792-5555  
Facsimile: (614) 792-5536

# FIRE RETARDING POLYPROPYLENE COMPOSITION

Inventor: Jerry Wagner

## BACKGROUND OF THE INVENTION

This application is a continuation of U.S. Application Serial No. 09/004,374, filed January 8, 1998, entitled Fire Retarding Polypropylene Composition, now U.S. Patent No. \_\_\_\_\_, issued \_\_\_\_\_.

5 This invention relates generally to fire retarding polymers, and more particularly to a fire retarding polypropylene.

In the manufacture of semiconductors, clean rooms must be used. The semiconductor chip processing equipment and other equipment in the clean rooms, such as wet benches, wafer storage cabinets, and the like, must meet certain flammability tests. Factory Mutual Research Corporation (FMRC) has proposed a flammability standard for clean room equipment, entitled "FMRC Clean Room Materials Flammability Test Protocol" (Rev. 2.0, February 1997) (the "FM 4910 Standard"). Recommendations pertaining to the instant invention are found in *Loss Prevention Data, Semiconductor Fabrication Facilities*, (Factory Mutual Engineering Corp., 1997), Section 2.4 Processing Tools and Product Storage. Section 2.4.1 of this publication requires that new wet benches and other processing tools be constructed of noncombustible materials. "Existing wet benches of combustible construction handling corrosive products should be replaced by wet benches in compliance with Section 2.4.1" (Section 2.4.3). "Noncombustible materials, or materials which are FMRC specification tested to meet the FMRC Clean Room Materials Flammability Test Protocol criteria should be used for mini-environment enclosures". (Section 2.4.6).

10  
15  
20

When there is a fire in a clean room, damage can occur from the fire, the smoke, and/or the corrosive combustion by-products. Even when the damage from the fire is minimal, the smoke and corrosive combustion by-products can ruin the products and the processing equipment and other equipment in the clean room. Thus, even a small fire can  
5 cause enormous monetary loss.

Materials which pass the FM 4910 Standard can be made into semiconductor chip processing equipment and clean room equipment without the necessity of providing additional fire detection and suppression equipment, also termed fixed fire protection. This is desirable because false alarms from fire equipment can result in lost wafer production, and  
10 consequently, monetary loss. Therefore, materials which pass the FM 4910 Standard are preferred for use in semiconductor chip processing equipment and clean room equipment.

Various materials have been used in the manufacture of semiconductor chip processing equipment and clean room equipment. Thermoplastic materials such as polyvinylidene fluoride (PVDF), perfluoroalkoxy (PFA), polyether ether ketone (PEEK), and  
15 polytetrafluoroethylene (PTFE) have been used. While these thermoplastics pass the FM 4910 Standard and therefore can be used without additional fire detection and suppression equipment, they are relatively expensive polymers.

Polyolefin materials, including polypropylene, have also been used for semiconductor chip processing equipment and clean room equipment. Polypropylene, FR-Polypropylene and  
20 PVC in semiconductor applications are not used for wetted parts or primary process chemical containment. These materials are used in corrosive wet tool construction as a structural material. They typically compose the plastic box that encloses the process vessels, chemical delivery systems, robots, etc. They also have the function of the process vapor containment and in some applications they are used in plenum drainage and also serve to provide short

term containment of process chemicals from process vessel failure. Contact with process fluids is either dilute, intermittent contact, i.e., plenum drainage, or it occurs as the result of splashing while filling process vessels or dripping while transferring wafer boats. The use of polyolefins is advantageous because they are inexpensive polymers. However, no fire retardant polyolefins have been able to pass the FM 4910 Standard. Consequently, fire detection and suppression equipment are required for semiconductor chip processing equipment and clean room equipment made of polyolefins.

Therefore, there is a need for an inexpensive, flame retarding polyolefin composition which will pass the FM 4910 Standard. The composition should be easily processable and capable of being formed into semiconductor chip processing equipment and clean room equipment. The composition should have the necessary physical properties so that it can be used to make the equipment.

#### BRIEF DESCRIPTION OF THE INVENTION

The present invention provides a flame retarding polypropylene composition (FRPP) that meets the fire resistance requirements for semiconductor clean room materials developed by FMRC in the FM 4910 standard. The composition resists fire propagation and limits smoke and corrosive combustion by products beyond the ability of previous fire retarding polyolefins. This eliminates the need for fire detection and suppression devices (fixed fire protection).

Polypropylene resin pellets and a surface treated magnesium hydroxide ( $Mg(OH)_2$ ) are thermoplastically mixed into pellets. The plastic pellets can then be extruded, compression molded or injection molded into the desired form. High loadings of magnesium hydroxide, greater than 50%, render polypropylene resistant to propagation of fire, smoke

and corrosive combustion by-products. Although high loadings of  $Mg(OH)_2$  ordinarily render polypropylene too brittle to use as construction material, this is avoided in the instant composition by using a surface treated  $Mg(OH)_2$ , Kisuma 5A, 5B, or 5J (Kyowa Chemical Industry Co. Ltd., Tokyo distributed in U.S. by Mitsui) as disclosed in Miyata et al., U.S.

5 Patent No. 4,098,762 and Miyata et al., U.S. Patent No. 4,145,404 , and a specialized reactor copolymer polypropylene resin in which ethylene-propylene rubber has been grafted onto the polypropylene chains to act as an interchain shock absorber. This results in a highly ductile material.

10 The composition of the instant invention meets all the requirements for Factory Mutual Listing for the FM 4910 Standard. The material exhibits extreme resistance to ignition and fire propagation and yields low smoke and corrosive combustion by-products. It is both impact resistant and rigid and thus ideal for structural materials. It has excellent thermoplastic weld strength and is machinable. It has both high impact resistance and high flex modulus.

15

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 represents a Corner Weld Strength Test Diagram of Compression Polymers.

Fig. 2 represents a Corner Weld Strength Test Sample Preparation Diagram.

Fig. 3 represents a Wet Deck Displaying Use of FRPP as Structural Material.

20

#### DETAILED DESCRIPTION OF THE INVENTION

A fire-retarding polypropylene composition is disclosed. The composition comprises a copolymer of polypropylene (Aristech TI4007, Aristech, Laporte, TX) and an ethylene/propylene rubber, and at least 50% but not greater than 60% by weight of a

magnesium hydroxide (Kisuma 5J, 5A or 5B, Kyowa Chemical Industry) coated with an anionic surface active agent, the magnesium hydroxide having (i) a strain in the  $\langle 101 \rangle$  direction of preferably not more than  $3.0 \times 10^{-3}$ , (ii) a crystallite size in the  $\langle 101 \rangle$  direction of preferably more than 800 Å, and (iii) a specific surface area, determined by the BET method, of preferably less than 20 mg<sup>2</sup>/g.

The copolymer preferably contains between about 80% and about 85% polypropylene and between about 15% and about 20% ethylene/propylene rubber. The copolymer is preferably reactor grade, i.e., made in a reactor as opposed to being compounded. The ethylene-polypropylene rubber has been grafted or spliced onto the polypropylene polymer chains with a catalyst that removes hydrogen atoms from polypropylene and substitutes ethylene propylene rubber which functions as an interchain shock absorber. The copolymer is preferably halogen free. The copolymer preferably contains polypropylene, but alternatively, polyethylene may be substituted. Properties of the fire retarding composition disclosed herein are shown in Table I. Figure 1 represents a corner weld strength test diagram which can be used to determine the corner weld strength in Table I, and Figure 2 represents a related corner weld strength test sample preparation diagram.

TABLE I

Composition Properties

<u>Property</u>	<u>Units</u>	<u>Value</u>	<u>ASTM Method</u>
Density	g/cc	1.36-1.38	D792
Tensile Strength	PSI	2,500	D638
Elongation at Yield	%	4.0	D638
Flex Modulus	PSI	450,000	D790
Izod Impact Notched 1/8 inch	ft-lb per inch	6.0	D256
Hardness Shore D	10 sec.	67	D785
Heat Deflexion Temp.	66 PSI	248°C	D648
Vicat Softening Pt.	1 kg	299°C	D1525
Corner Weld Strength	lb/linear inch	570	CPG Weld Test
Water Absorption (7 d. at 122°)	%	<0.07	D570
Coefficient of Expansion	in/in/°F	$6.6 \times 10^{-5}$	D696
Flame Classification	FPI	4.4	FM 4910 Protocol
	SDI	0.2	Clean Room
	CDI	0.6	Listing Report Values
	TRP	570	
Flame Classification	ETL Labs	V-0	UL 94 Test
	ETL Labs	5VA	UL 94 Test
	ETL Labs	<25 flame	E84 Tunnel Test
	ETL Labs	<100 smoke	meets Class A

Listing Report FMRC #3D7Q7, July 5, 1997.

- 5 A fire retarding semiconductor apparatus passing the FMRC Clean Room Materials Flammability Test Protocol is also disclosed. The apparatus comprises a polymer and a magnesium hydroxide composition, the composition comprising a copolymer of polypropylene and an ethylene/propylene rubber, and at least 50% but not greater than 60% by weight of a magnesium hydroxide coated with an anionic surface active agent, the
- 10 magnesium hydroxide having (i) a strain in the <101> direction of not more than  $3.0 \times 10^{-3}$ , (ii) a crystallite size in the <101> direction of more than 800 Å, and (iii) a specific surface area, determined by the BET method, of less than 20 mg<sup>2</sup>/g. The minimum Notched Izod Impact using ASTM D256 test is 0.5 ft. per pounds per inch. The rubber modified polypropylene

and the uniform particle size of the magnesium hydroxide used in the invention, form an extremely uniform geometry of plastic and dispersed mineral resulting in a highly ductile material.

A method for producing a fire retarding polypropylene composition which passes the FMRC Clean Room Material Flammability Test Protocol is also disclosed. The method includes mixing a copolymer of polypropylene and an ethylene/propylene rubber with at least 50% but not greater than 60% by weight of a magnesium hydroxide coated with an anionic surface active agent, the magnesium hydroxide having (i) a strain in the  $\langle 101 \rangle$  direction of not more than  $3.0 \times 10^{-3}$ , (ii) a crystallite size in the  $\langle 101 \rangle$  direction of more than 800 Å, and (iii) a specific surface area, determined by the BET method, of less than 20 mg<sup>2</sup>/g at a temperature above a melting point of the copolymer to form a blend. The method preferably includes processing the blend by extrusion, injection molding, or compression molding into articles adapted to be used in a clean room, such as maintenance cleaning benches, water storage cabinets, or building panels.

Polymers which pass the FM 4910 Standard typically have high limiting oxygen indexes, (LOI), greater than 45. The typical method of fire retarding polyolefin materials is to add gas phase FR's that increase the LOI. These Gas Phase FR's bind up the available oxygen in the area surrounding the fire, thereby starving the flames of oxygen. Supporting this theory, PVDF and PFA, which have LOIs of about 100, and ethylene-trifluorethylene (ECTFE), which has an LOI of about 60, pass the FM 4910 Standard. Polyvinylidenefluoride (PVDF), which has an LOI of 45 is on the borderline, while ethylene-trifluoroethylene (ETFE), which has an LOI of 38, does not pass. Polypropylene and the fire retarding polypropylene which has been used in the past, which have LOIs in the range of about 30-35, also do not pass. The FR polypropylene materials burn rather severely. As a result, it was



believed that only materials which have a high LOI would pass the FM 4910 Standard. It was also believed that FR polypropylene would not pass because of its low LOI.

The fire retarding polypropylene of the present invention has an LOI of about 30. Therefore, based upon the gas phase theory and previous experience, it would be expected that this material would not pass the FM 4910 Standard. However, surprisingly, the fire retarding polypropylene of the present invention does pass, and it has excellent fire performance properties. It conducts heat away from the surface very rapidly. In addition, it releases water during decomposition which cools the surface. This gives the composition a very high resistance to ignition and fire propagation. The composition also forms an extremely efficient char layer which inhibits the propagation of flames. The high loading of magnesium hydroxide gives the composition a very stiff melt viscosity which prevents tearing open of the char layer in a fire. This combination of properties allows the fire retarding polypropylene of the present invention to pass the FM 4910 Standard.

The fire retarding polypropylene of the present invention utilizes a unique magnesium hydroxide. The magnesium hydroxide, which is described in U.S. Patent No. 4,098,762, to Miyata et al., is commercially available from Kyowa Chemical Industry Co., Ltd. under the name Kisuma 5A, 5B, or 5J. Kisuma 5J is preferred in the present invention. Magnesium hydroxide is typically used as a secondary fire retardant for smoke suppression in conjunction with other fire retardants. It is rarely used as the primary fire retardant in a polymer system because it does not increase the LOI of the material. However, it was discovered that incorporating high levels of the patented magnesium hydroxide (over about 50% by weight) renders polypropylene extremely resistant to the propagation of fire, smoke, and corrosive combustion by-products in a fire situation.

The level of magnesium hydroxide is preferably in the range of between about 50% and about 60% by weight. Below about 50%, the material does not pass the FM 4910 Standard. When the level exceeds about 60% by weight, it becomes difficult to process the material.

5           The use of such high loadings of magnesium hydroxide in polypropylene would normally produce a material so brittle that it could not be used as an equipment construction material. However, the combination of the patented magnesium hydroxide and a particular type of polypropylene produces a highly ductile material which can be used for equipment construction. The polypropylene is a copolymer of polypropylene and an ethylene/propylene rubber. The ethylene/propylene rubber, which is grafted onto the polypropylene polymer chains, acts as an interchain shock absorber. Among the polypropylene copolymers which can be used in the present invention are Aristech TI4007 from Aristech and Amoco 3045 from Amoco Chemical Co.

10  
15           The polypropylene pellets and the magnesium hydroxide are intensively mixed and formed into pellets. The pellets can be extruded, injection molded, or compression molded into plastic sheet or other geometric shapes for use in semiconductor chip processing equipment and other semiconductor clean room equipment. The processing can be done using standard plastic fabricating equipment. The following example illustrates the compression molding method of the invention.

## EXAMPLE I

### Method for Compression Molding Composition to Form a Sheet 1¼ Inches Thick (Net Weight 288 lbs.)

- 5            1.        Materials are heated in a mold at increasing temperatures for approximately six (6) hours at the following temperatures and pressures:

<u>Temperature (°F)</u>	<u>Pressure (ft./lbs. psi)</u>	<u>Length of Time (Hrs:Mins)</u>
365	500	1:10
370	600	1:20
375	300	3:30

2.        Materials are cooled in the mold by running cool oil through the mold at a pressure of 1200 ft.-lbs psi.

10           3.        The sheet can then be cut and formed into equipment, such as wet benches and storage cabinet. The pieces can be bonded together using many thermoplastic welding techniques.

The composition of the invention can also be used in the construction of semiconductor chip processing equipment and semiconductor clean room items such as maintenance cleaning benches, water storage cabinets and wall and ceiling panels. Figure 3 represents a wet deck that uses FRPP of the present invention as a structural material.

However, the preferred system herein described is not intended to be exhaustive or to limit the invention to the precise forms disclosed. They are chosen and described to explain the principles of the invention, and the application of the method to practical uses so that others

20        skilled in the art may practice the invention.